Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Sintering mechanism and microwave dielectric properties of $BaTi_4O_9$-BBZ composite for LTCC technology

Haishen Ren[a,b,*], Tianyi Xie[a,c], Mingzhao Dang[a,b], Shaohu Jiang[a], Huixing Lin[a], Lan Luo[a]

[a] *Key Laboratory of Inorganic Functional Material and Device, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*
[c] *Department of materials, Chongqing University of Technology, Chongqing 400050, China*

ARTICLE INFO

Keywords:
BaO-B_2O_3-ZnO glass
$BaTi_4O_9$ ceramic
Sintering mechanism
Dielectric properties

ABSTRACT

A low temperature co-fired ceramic (LTCC) material was fabricated by mixing $BaTi_4O_9$ ceramic with BaO-B_2O_3-ZnO (BBZ) glass. The sintering mechanism was further analyzed through the wetting behavior, activation energy, phase evolution, microstructure and microwave dielectric properties of the $BaTi_4O_9$-BBZ composite. The results show that the sintering temperature of the $BaTi_4O_9$ ceramics can be significantly lowered from 1300 to 925 °C by the BBZ glass. This is due to the three-stage partially reactive liquid assisted sintering process which consists of glass redistribution and local grains rearrangement, solution-reprecipitaion including glass crystallization and reactions between the glass and ceramic, and global grain rearrangement, closure of pores and viscous flow. XRD patterns exhibit that $BaTi_4O_9$ reacts with the crystallization phase of BBZ glass obviously during sintering to form two new phases $BaTi(BO_3)_2$ and $Ba_4Ti_{13}O_{30}$. The activation energy of $BaTi_4O_9$ ceramic is calculated to be 520.9 ± 40.46 kJ/mol, while that of $BaTi_4O_9$-BBZ composite is reduced to 330.98 ± 47.34 kJ/mol. With increasing sintering temperature, the dielectric constant (ε_r) and the quality factor (Q×f) value increases firstly and then decreases, and the temperature coefficient of resonant frequency (τ_f) value slightly decreases. Typically, the $BaTi_4O_9$ -BBZ composite sintered at 925 °C for 2 h displays excellent microwave dielectric properties of ε_r = 26.4, Q×f = 27300 GHz and τ_f = + 0.3 ppm/°C. In addition, the good chemical compatibility of this material with Ag electrode makes it as a potential candidate for LTCC technology.

1. Introduction

Low-temperature co-fired ceramics (LTCC) technology has played a more and more important role in the development of mobile and satellite communications, radar systems, global position systems (GPS) and wireless area network (WLAN) technology since it can meet the requirements of miniaturization, integration and high reliability of electronic devices [1,2]. There are several features for ideal LTCC materials [1–3]: sintering temperatures lower than 950 °C, an appropriate dielectric constant (ε_r), high quality factor (Q×f), a near-zero temperature coefficient of resonant frequency(τ_f), and the excellent chemical compatibility with Ag inner electrodes. Unfortunately, most of the commercial dielectric ceramics with good microwave dielectric properties cannot be used for LTCC application due to the high sintering temperatures above 1200 °C. One of the most important focal problems for the development of LTCC materials is to lower the sintering temperature and maintain the excellent dielectric properties of the ceramics as much as possible.

$BaTi_4O_9$ is a well-known commercialized dielectric ceramic with dielectric constant of approximately 37–39 and quality factor (Q×f) of 21,000–37,000 GHz and sintering temperature of it is around 1300 °C [4–6]. On the other hand, $BaTi_4O_9$ ceramics have a large temperature coefficient of resonant frequency (+15 ppm/°C). To meet the requirements for LTCC, large amount of work has been done to lower the sintering temperature by adding low-melting glasses or compounds [7–11]. However, it is easy for $BaTi_4O_9$ to react with the low-melting additive, and the reaction products may have an effect on its microwave dielectric properties. Chu [8] et al. found that CuB_2O_4 and $BaCuB_2O_5$ additives can decrease the sintering temperature of the $BaTi_4O_9$ ceramics below 950 °C, but the new formed phases $BaTi_5O_{11}$ and $Ba_4Ti_{13}O_{30}$ deteriorate the Q×f value and cause the rising of τ_f. Gormikov and Belous [9,10] reported that ZnO not only can effectively lower the sintering temperature of the $BaTi_4O_9$ ceramic to 1200 °C but also turn the positive τ_f value to near-zero due to the formation of the second phase $BaZn_2Ti_4O_{11}$. Kim [11] et al. pointed out that the microwave dielectric properties of low temperature fired $BaTi_4O_9$ ceramic are dependent on the content of the ZnO-B_2O_3 glass additive, which determines the crystalline phases present and the microstructure after processing. Therefore, selecting a proper sintering aid for $BaTi_4O_9$

* Corresponding author at: Key Laboratory of Inorganic Functional Material and Device, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.
E-mail address: renhaichen@student.sic.ac.cn (H. Ren).

http://dx.doi.org/10.1016/j.ceramint.2017.06.178
Received 29 May 2017; Received in revised form 26 June 2017; Accepted 28 June 2017

ceramics to lower the sintering temperature below 950 °C as well as improve the τ_f is of critical importance for the LTCC application.

BaO-B_2O_3-ZnO glass system with a low softening temperature of 480–560 °C exhibits great potential as candidates for LTCC applications [12]. In our previous studies, the sintering temperature of $Ba_2Ti_9O_{20}$ ceramics has been successfully lowed from 1400 °C to around 900 °C by using a glass from BaO-B_2O_3-ZnO (BBZ) system [13]. It was found in these studies that the BBZ glass additive had an enhancement effect upon the quality factor (Q×f) of $Ba_2Ti_9O_{20}$ ceramics, instead of degradation one as found in usual cases when low melting glass additive is involved. The BBZ glass has also been proved to be a negative τ_f -tailoring material to $Ba_2Ti_9O_{20}$, and it can make the positive τ_f value of the ceramic shift to negative as the amount of the glass increased. Long [14] et al. reported a similar result, in which a BaO-B_2O_3-ZnO (BBZ) glass was used as a sintering aid of $BaNd_2Ti_4O_{12}$ ceramics, and the densification temperature of it had been lowered from 1450 to 900 °C, and the τ_f values decreases gradually with increasing the amount of BBZ glass. Therefore, it is believed that the BBZ glass might act as an effective τ_f-tailoring material for $BaTi_4O_9$ ceramic adjusting the τ_f value to near-zero as well as be a kind of effective sintering aid for reducing the sintering temperature of $BaTi_4O_9$ ceramic to below 950 °C. In this paper, a LTCC material based on $BaTi_4O_9$ ceramic powder with BBZ glass is fabricated, and the phase composition, sintering process, wetting behavior, activation energy, microstructure and microwave dielectric properties of the material are investigated.

2. Experiments

The $BaTi_4O_9$ power was synthesized by conventional solid-state reaction method using reagent grade $BaCO_3$ (99.0%) and TiO_2 (99.0%) as starting powders. $BaCO_3$ and TiO_2, with molar ratio of 1:4, were mixed in a plastic bottle using distilled water and ZrO_2 balls as media by planetary ball mill for 2 h. The mixture was then dried at 150 °C for 12 h and calcined at 1150 °C for 4 h to form $BaTi_4O_9$ phase. The BBZ glass with the molar composition of 30 BaO-40 B_2O_3−30 ZnO was prepared by a conventional glass fabrication process: reagent grade powders of H_3BO_3 (99.9%), $BaCO_3$ (99.0%), and ZnO (99.5%) were weighed as the raw materials. The glass batch about 300 g was melted in a platinum crucible at 1250 °C for 2 h, and then the melts were quenched in water. The quenched glass was planetary-milled in aluminum jar with ethyl alcohol and ZrO_2 balls for 2 h. After being dried and screened through a 200-mesh sieve, the BBZ glass powder was obtained. Then, $BaTi_4O_9$ was mixed with 27.5 wt% of BBZ glass powders and milled with ZrO_2 balls and ethyl alcohol for 2 h. After drying, the mixture was granulated by adding 8 wt% poly(vinyl butyral) (PVB) solution for getting the uniformity particle size and good fluidity power. Preformed pellets of 15 mm in diameter and 7–8 mm in height were obtained from the powder using a cylindrical steel mold, and then were pressed at 2 MPa by hydraulic pressing, followed by sintering between 905 and 955 °C for 2 h in air at a heating rate of 5 °C/min.

Differential scanning calorimetry (DSC) scan of 20 mg of glass powders was run on a computerized system (NETZSCH DSC 404 C) at 10 K/min from ambient temperature to 1000 °C. Shrinkage value of the sample was measured with a horizontal-loading dilatometer with alumina rams and boats (DIL 402 C, Netzsch Instruments, Germany) with different heating rate of 5, 10 and 15 K/min, respectively. The bulk densities of the sintered samples were measured by the Archimedes method. The crystal phases present in sintered samples were identified by X-ray diffraction analysis (XRD, Uitima, Rigaku, Japan) using CuKα radiation, and were further analyzed by energy dispersive spectroscopy (EDS). The microstructures of sintered samples were observed by field emission scanning electron microscope (FESEM, Magellan 400, FEI Company, USA). The dielectric constant (ε_r) and the Q value of the sintered samples which were processed into disks 12 mm in diameter and 6 mm in height were measured in the TE011 mode by the Hakki and Coleman method, using an Agilent E8363A PNA series network analyzer in frequency range of 1–20 GHz. The temperature coefficient of resonant frequency (τ_f) was measured over the range from 25 to 85 °C, defined as follows:

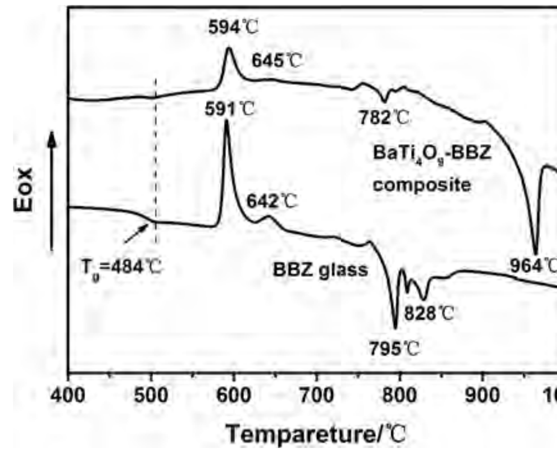

Fig. 1. DSC curves of the BBZ glass and 27.5 wt% BBZ doped $BaTi_4O_9$ ceramic at 10 K/min heating rate.

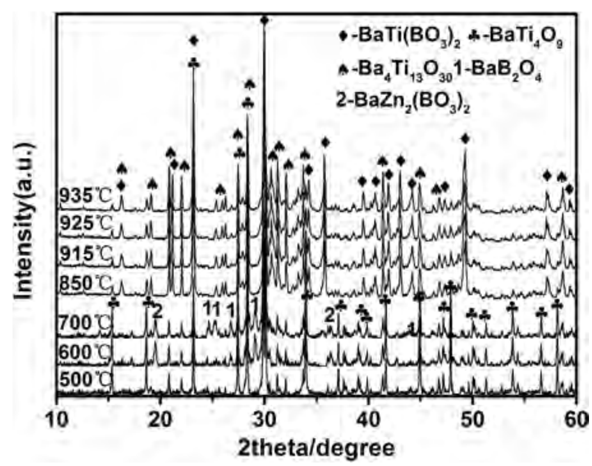

Fig. 2. XRD patterns of the $BaTi_4O_9$-BBZ composite sintered at different temperatures for 2 h.

$$\tau_f = (f_{85} - f_{25})/(60\times f_{25}) \times 10^6 (ppm/°C) \quad (1)$$

where f_{85} and f_{25} represent the resonant frequencies at 85 °C and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows DSC curves of the BBZ glass and the $BaTi_4O_9$-BBZ composite at heating rate of 10 K/min. In the DSC curve of the BBZ glass, the glass transition temperature (T_g) at 484 °C is recorded firstly. Two evident exothermic peaks of crystallization (T_p) at 591 °C and 642 °C may be related to the formation of BaB_2O_4, $BaZn_2(BO_3)_2$ and unknown phase on the basis of the XRD results in the supplemental material. Three endothermic peaks are recorded between 795 °C and 828 °C corresponding to the melting point (T_m), which implies that the BBZ glass could provide a large amount of liquid phase at low temperature and facilitate the densification process according to the liquid-phase sintering mechanism. Compared with the BBZ glass, the addition of $BaTi_4O_9$ to BBZ glass has almost no variation in the glass transition temperature, crystallization temperature and the melting point; however, another melting point locating at 964 °C are detected.

The XRD patterns of the $BaTi_4O_9$-BBZ composite sintered at the various temperatures ranging from 500 to 935 °C for 2 h are shown in

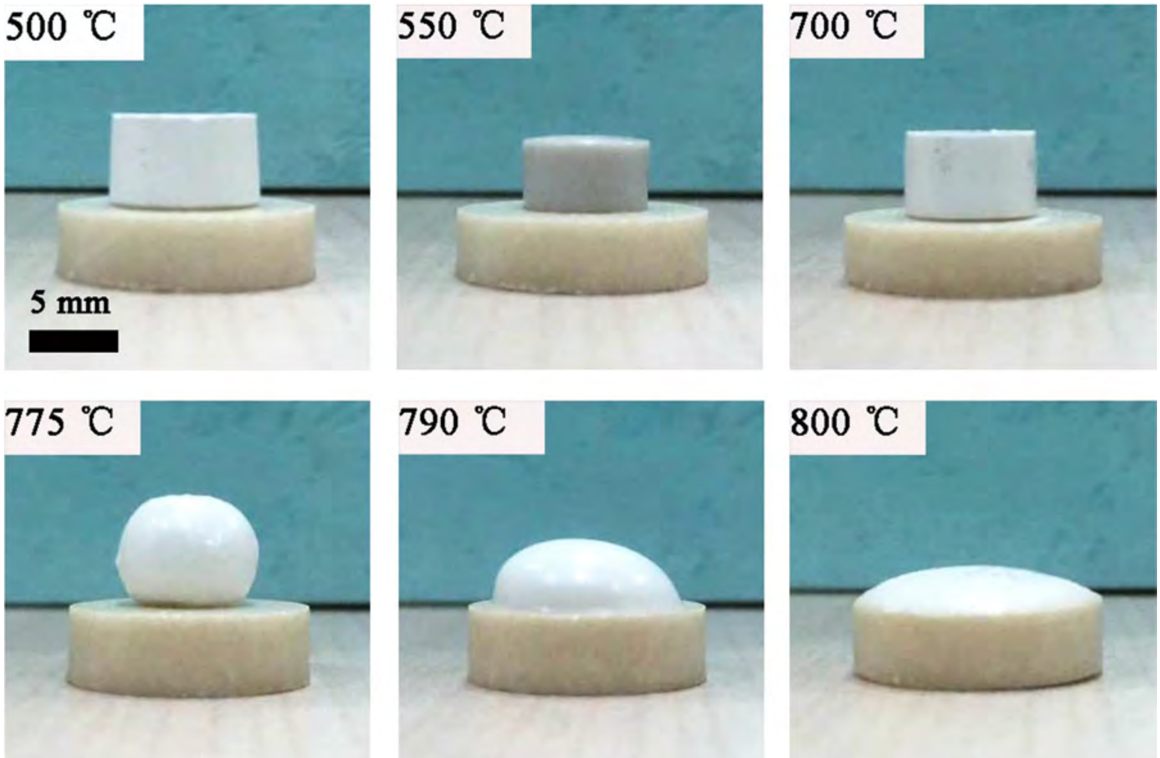

Fig. 3. Wetting behavior of BBZ glass on the dense $BaTi_4O_9$ substrate at different temperatures.

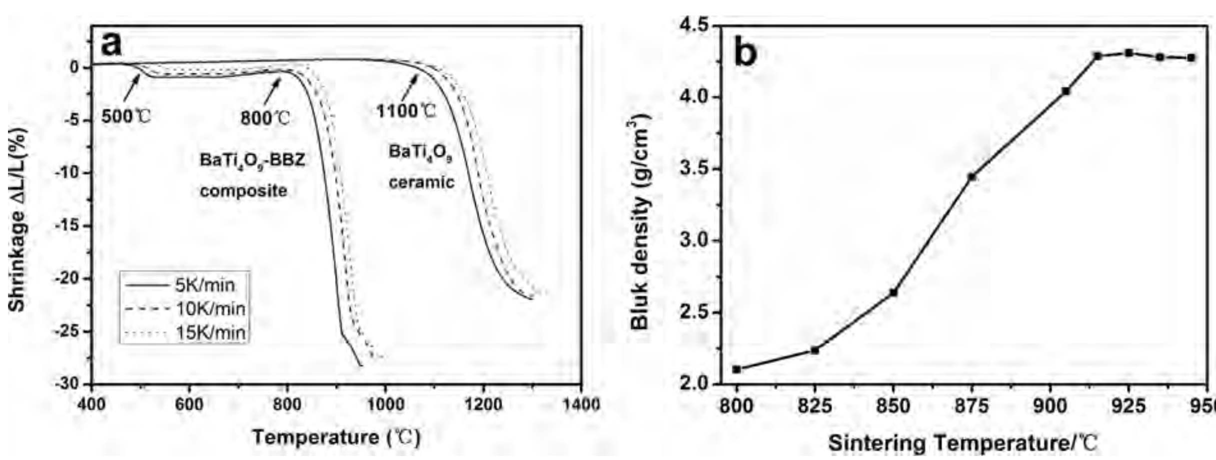

Fig. 4. (a) Liner shrinkage curves of the pure $BaTi_4O_9$ ceramic and the $BaTi_4O_9$-BBZ composite at different heating rates of 5, 10 and 15 K/min. (b) Bulk density of the $BaTi_4O_9$-BBZ composite sintered at different temperatures for 2 h.

Fig. 2. The XRD pattern of the sample sintered at 500 °C reveals that there is only $BaTiO_4$ phase and a little $Ba_4Ti_{13}O_{30}$ phase. As temperature increases from 600 to 750 °C, crystallization phases of BBZ glass, BaB_2O_4, and $BaZn_2(BO_3)_2$, are also identified in sample except for $BaTiO_4$ and $Ba_4Ti_{13}O_{30}$, which proves that the $BaTi_4O_9$ ceramic has no influence on the crystallization behavior and its crystallization temperature. At 850 °C, the main phase of composites transforms $BaTi_4O_9$ into $BaTi(BO_3)_2$ phases, the crystallization phases of BBZ glass disappear and the diffraction intensity of $Ba_4Ti_{13}O_{30}$ become stronger compared to low temperature. Combination of the DTA results, it can be concluded that both BaB_2O_4 and $BaZn_2(BO_3)_3$ are melted about 800 °C and the liquid phase reacts with $BaTi_4O_9$ phase leading to the formation of $BaTi(BO_3)_2$ and the increasing of $Ba_4Ti_{13}O_{30}$. That is to say that $BaTi_4O_9$ ceramic does not directly react with the glass but with the crystallization phase of glass. On the other hands, there are no additional peaks observed when the sintering temperature increased from 850 to 945 °C, which means that the phase composition has no variations after sintering at 850 °C. Besides, Jean et al. [15] reported that the sintering process of glass/ceramic system can be classified as nonreactive, partially reactive, and completely reactive systems depending on the reactivity between glass and ceramic. For our study, the sintering process of the $BaTi_4O_9$/BBZ system is the partial reaction type. These chemical reactions during sintering may be expressed as following,

$$BBZ\,glass \xrightarrow[crystallization]{} BaB_2O_4 + BaZn_2(BO_3)_2 \tag{2}$$

$$BaTi_4O_9 + melting - B_2O_3 \rightarrow BaTi(BO_3)_2 + Ba_4Ti_{13}O_{30} \tag{3}$$

For the study of BBZ wetting behavior, a piece of green BBZ glass compact with 9.2 mm in diameter and 5.5 mm in height is placed on top of the dense $BaTi_4O_9$ substrate and followed by sintering between 550 and 800 °C at a heating rate of 10 K/min recorded by an optical camera as shown in Fig. 3. It can be found that the BBZ glass cylinder slightly shrinks at 550 °C. However, there is just a slight expansion of

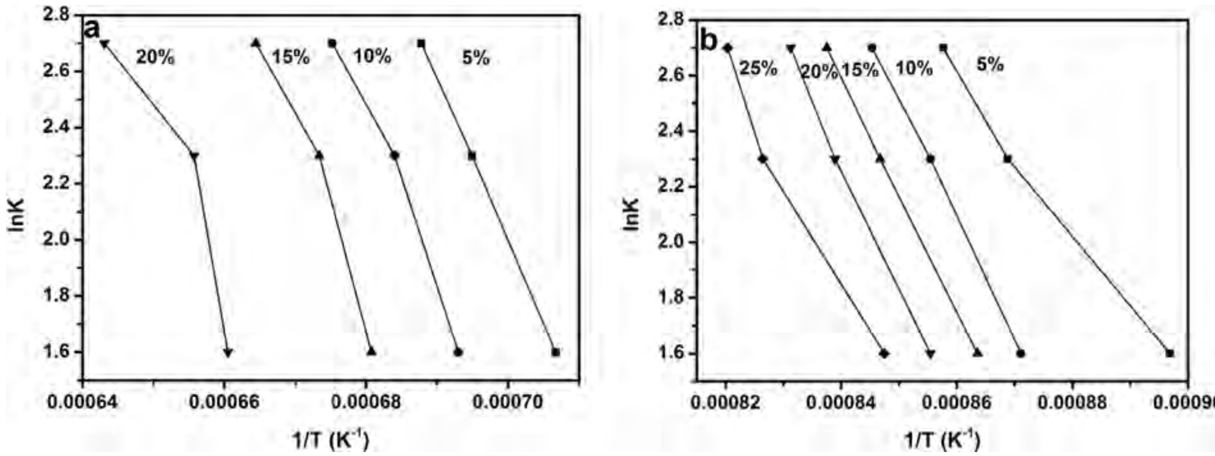

Fig. 5. Sintering rate (ln k) plotted against the inverse of temperature (1/T) for the pure $BaTi_4O_9$ ceramic (a) and the $BaTi_4O_9$-BBZ composite (b) at a given shrinkage values.

Table 1
The activation energy of pure $BaTi_4O_9$ ceramic and $BaTi_4O_9$-BBZ composite at a given shrinkage values.

Shrinkage dL/L (%)	Activation energy of $BaTi_4O_9$ (KJ/mol)	Activation energy of $BaTi_4O_9$-BBZ (KJ/mol)
5	482.49	233.15
10	514.36	354.88
15	561.67	351.27
20	525.17	378.29
25		337.33
Average	520.9 ± 40.46	330.98 ± 47.34

glass cylinder at 700 °C, and the expansion becomes more obvious with the increase of sintering temperature. It may be due to the expansion of closed pores at high sintering temperature [16]. The wetting angle between the molten glass and $BaTi_4O_9$ substrate is greater than 90 ° at 775 °C, which indicates that the glass cannot wet the ceramic particles. When the sintering temperature is higher than 790 °C, the wetting angle is less than 90 °, suggesting that the glass addition could wet the $BaTi_4O_9$ ceramic particles at temperature higher 790 °C. The shrinkage and wetting temperature agree well with the T_g and T_m of BBZ glass determined by DSC shown in Fig. 1.

Fig. 4a shows the linear shrinkages curves of the pure $BaTi_4O_9$ ceramic and the $BaTi_4O_9$-BBZ composite at different heating rates of 5, 10 and 15 K/min. The shrinkage of pure $BaTi_4O_9$ ceramic start at 1100 °C, while the onset of shrinkage dramatically decreases to about 500 °C for BBZ doped $BaTi_4O_9$ ceramic. However, a platform occurs after 580 °C probably due to the beginning of the BBZ glass crystallization process that retards the further shrinkage of composite. This stage has begun at about 580 °C and last till about 800 °C on the basis of the DCS results shown in Fig. 1. At this temperature, the liquid phase appears because of the melting of BaB_2O_4 and $BaZn_2(BO_3)_3$, which results in the direct shrinkage of sample after 800 °C. The results indicate that the crystallization of glass in the early stage retards the

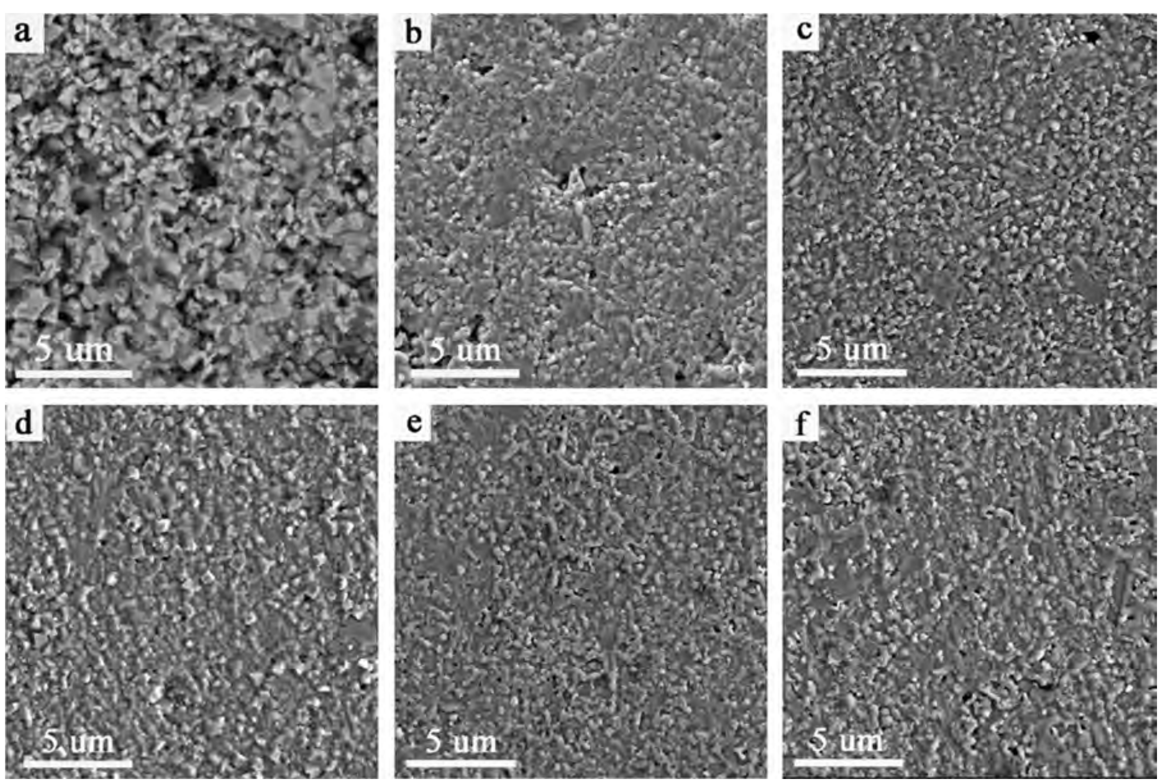

Fig. 6. SEM micrographs of the $BaTi_4O_9$-BBZ composite sintered at 800 °C (a), 900 °C (b), 915 °C (c), 925 °C (d), 935 °C (e) and 945 °C (f) for 2 h.

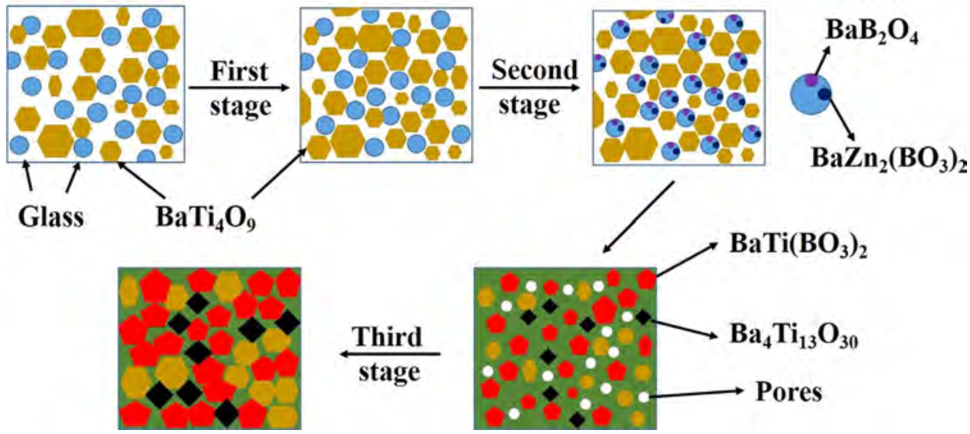

Fig. 7. Schematic diagram showing the sintering process of the $BaTi_4O_9$-BBZ composite.

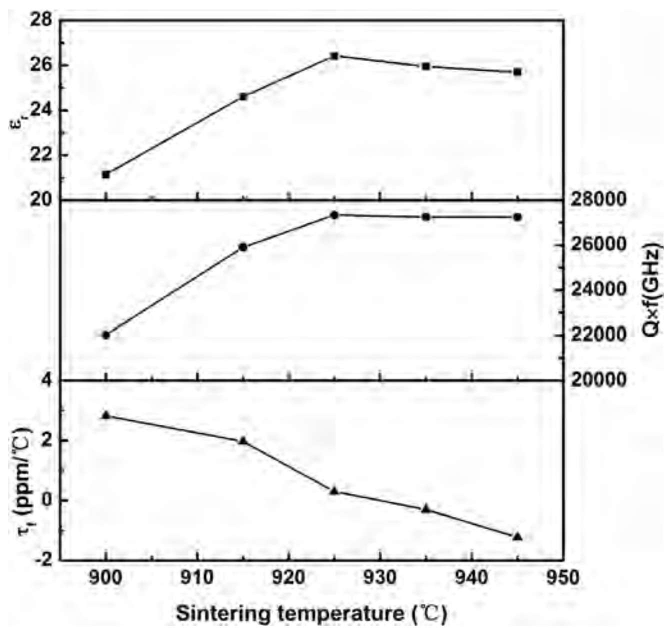

Fig. 8. Microwave dielectric properties of the $BaTi_4O_9$-BBZ composite as a function of the sintering temperature.

shrinkage and the formation of liquid phase promotes the rapid shrink. The whole sintering process of composite agrees well with the wetting behavior of BBZ glass on the dense $BaTi_4O_9$ substrate as shown in Fig. 3. These observations are further supported by the bulk density of sintered at from 800 to 945 °C for 2 h in Fig. 4b. It can be seen that the bulk density depends strongly on the sintering temperature. The bulk density of sample sintered at 800 °C is only 2.2 g/cm^3. When the sintered temperature rises from 800 to 925 °C, the bulk density of the composite increases to 4.31 g/cm^3. It is consistent with a rapid shrink of composite after 800 °C owing to the appearing of liquid phase. But the bulk density of sample starts to decrease after 925 °C. This may have been caused by abnormal grain growth and the formation of pores due to excessive firing. This result suggests that the composite can be well sintered at 925 °C and has a maximum bulk density of 4.31 g/cm^3.

To further understand the sintering behavior, the activation energy (Ea) of the pure $BaTi_4O_9$ ceramic and the $BaTi_4O_9$-BBZ composite can be calculated by applying the follow Arrhenius equation [17]:

$$lnk = -E_a/R(1/T) + lnz \quad (4)$$

where ln k is the sintering rate, Ea the activation energy, T the absolute temperature, R the universal gas constant (=8.3145 J/K/mol) and ln z a constant. Ea values are obtained by plotting ln k vs 1/T. Fig. 5 show the ln k plotted against 1/T for the pure $BaTi_4O_9$ ceramic and the $BaTi_4O_9$-BBZ composite at a given shrinkage values (dL/L), 5%, 10%, 15%, 20% and 25% according to Fig. 4a. After calculated from the dilatometric curves, an average Ea of about 520.9 ± 40.46 kJ/mol for pure $BaTi_4O_9$, and an average Ea of about 330.98 ± 47.34 kJ/mol for $BaTi_4O_9$-BBZ are obtained (Table 1), which means that the activation energy is significantly lowered when $BaTi_4O_9$ sintering at low temperature doping with BBZ. It is similar with the report [18] that the liquid-phase sintering mechanism enhanced the sintering process should lead to a decrease of the Ea.

Fig. 6 shows that the SEM micrographs of the $BaTi_4O_9$-BBZ composite sintered at temperatures ranged from 800 to 945 °C for 2 h. At lower sintering temperature (800 °C), there are a large amount of open-pores and the liquid phase obtained from the melting of BaB_2O_3 and $BaZn_2(BO_3)_2$ partially encapsulates the ceramic particles in composite (Fig. 4a). The microstructures of composite become more compact and the grains become larger with the sintering temperature

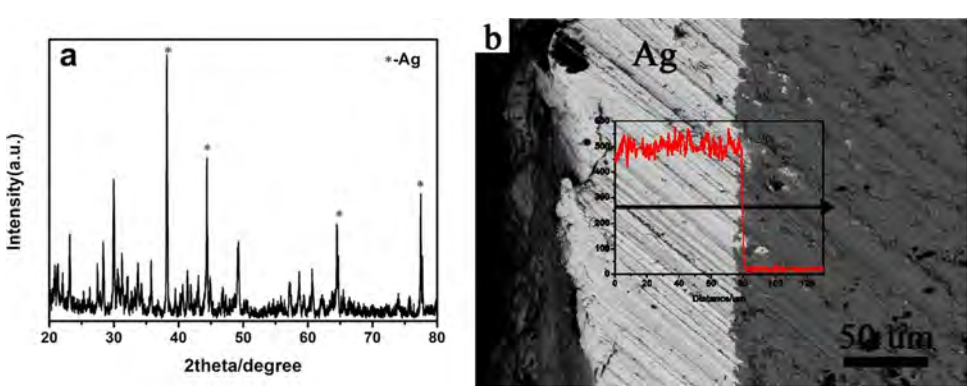

Fig. 9. XRD pattern (a), SEM and EDS line scan (b) of the cross-section of the $BaTi_4O_9$-BBZ composite co-fired with Ag electrode at 925 °C for 2 h.

increased from 900 to 925 °C presented in Fig. 4b–d. In combination with the liner shrinkage and bulk density results, it can be inferred that the rapid increase of the bulk density sintered at from 800 to 900 °C may be related to the elimination of substantial pores and the slight increase after 900 °C may be related to the growth of grains. However, as the sintering temperature further rises up to 935 °C and 945 °C, abnormal grain growth can be observed and pores occur again (Fig. 4e-f) which leads to the dropping of the bulk density.

It was reported that the reactive liquid-phase sintering process (LASP) is achieved by a three-stage sintering process, consisting of rearrangement, solution-reprecipitation, and solid-state sintering, whereas the non-reactive LASP including glass redistribution and local grain rearrangement, global grain rearrangement and closure of pores, and viscous flow [19]. Either reactive or non-reactive LASP, sufficient liquid phase, the solubility of ceramic in liquid phase and a good wetting behavior of the liquid phase with ceramic are essential factors in sintering process [20]. As discussed in previous analysis, there are a big amount of liquid phase obtained from the melting of crystallization phase, Ba and Ti ions from $BaTi_4O_9$ ceramic will be concurrently dissolved out into the boron melt [21], and the melt can well wet the ceramic particles at higher than 790 °C, which point out that the above mentioned conditions of LASP are satisfied. However, these behaviors on crystallization process, the melting and reaction in the early stage of sintering make the present reactive LASP more complex than the conventional one that shrinkage process almost finishes before the crystallization process and/or reaction happen in the later stage of sintering [16,22,23].

Combination of the analysis of above results, the sintering process of the $BaTi_4O_9$/BBZ composite in our study can be summarized as Fig. 7 without taking account of the shape of the glass and the crystalline phases. The first stage of the sintering process begins at the BBZ glass transition temperature about 500 °C when the glass begins to turn into viscous fluid, which leads to glass redistribution, local particles rearrangement, and a handful of pores' elimination. The driving force for this process is produced by the transformation of glass state and only slight shrinkage occurs in this stage according to the results of Fig. 3 and Fig. 4a. The second stage is characterized by the crystallization processes of the BBZ glass, the melting of crystallization phase and reaction between the melts and ceramic. The shrinkage is almost zero and swelling even happens in the late of this stage. The reason may be the rapid raising of glass viscosity after the crystallization processes and repulsion forces among solid particles because of a non-wetting behavior between the melt and ceramic [19]. At the last stage, the rest liquid phase has filled the gaps among ceramic grains by reaction and then those ceramic grains are taut to slide, rearrange and form a more compact structure (shown in Fig. 4b) by the capillary force of a liquid-phase-filled cylindrical pore channel. At the same time, the grain growth (shown in Fig. 4d) credits to the grain boundary migration and the grains reprecipitation from the small grains to the adjacent large ones as the sintering temperature increases. The above results indicate that the densification of $BaTi_4O_9$/BBZ composite can be achieved by three-stage partially reactive liquid assisted sintering process, consisting of glass redistribution and local grains rearrangement, solution-reprecipitaion including glass crystallization and reactions between the glass and ceramic, and global grain rearrangement, closure of pores and viscous flow. The main shrinkage occurs in the last stages.

Fig. 8 shows the dielectric constants, Q ×f values and the τ_f values of the $BaTi_4O_9$-BBZ composite sintered at 900–945 °C for 2 h. The variation of the dielectric constants and the Q ×f values with respect to temperature has a similar tendency with density shown in Fig. 4b. The dielectric constants and the Q ×f values of composites rise first with increasing temperature to a maximum value of 26.4 and 27,300 GHz at 925 °C, respectively. After 925 °C, the decrease in the dielectric constant and the Q ×f value might be as a reason of an abnormal grain growth and the formation pores (shown in Figs. 6e and 6f) duo to over-sintering. The τ_f values slightly decrease with the increasing sintering temperature. The excellent dielectric properties of ε_r = 26.4, Q×f = 27,300 GHz and τ_f = + 0.3 ppm/°C are achieved when the composites is sintered at 925 °C for 2 h.

In order to confirm the chemical compatibility of the $BaTi_4O_9$-BBZ composite with Ag electrode, the silver plate (Shanghai Miracle Materials Technology Co. LTD.) was printed on the surface of the preformed pellets by 200 mesh sieve then sintered at 925 °C for 2 h. The Fig. 9 shows XRD pattern, SEM micrograph and EDS line scan of the composite co-fired with Ag electrode. The XRD pattern shows only cubic silver phase (JCPDS file no. 04–0783) and no another phases of silver compounds in the sample, which indicates that no chemical reaction has taken place between the low-sintering ceramic and silver. Meanwhile, it is can be observed that there is a clear interface between the low-sintering ceramic and the electrode, as shown in Fig. 9b. And EDS line scan shows that Ag diffusion no occur during the co-fired processing. Combining the excellent microwave dielectric properties, it can be proposed that the $BaTi_4O_9$-BBZ composite is a very promising candidate material for the LTCC applications.

4. Conclusions

In this study, the effect of BBZ glass on the sintering mechanism, phase evolution, microstructure and microwave dielectric properties of the $BaTi_4O_9$-BBZ composite was investigated. The main processes of the $BaTi_4O_9$-BBZ is disclosed by the chemical reactions between $BaTi_4O_9$ and the BBZ glass and the sintering process, which is called three-stage partially reactive liquid assisted sintering process, consisting of glass redistribution and local grains rearrangement, solution-reprecipitaion including glass crystallization and reactions between the glass and ceramic, and global grain rearrangement, closure of pores and viscous flow. The results showed the fact that the BBZ glass significantly decreases the sintering temperature of the $BaTi_4O_9$ ceramics to less than 950 °C. XRD patterns revealed that two new phases $BaTi(BO_3)_2$ and $Ba_4Ti_{13}O_{30}$ are found in the material. The sintering activation energy of $BaTi_4O_9$ ceramic is reduced from 520.9 to 330.98 kJ/mol by adding the BBZ glass additive. The sintering temperature affects the microwave dielectric properties of $BaTi_4O_9$-BBZ composites. It was found that $BaTi_4O_9$-BBZ composite sintered at 925 °C for 2 h reaches a maximum density of 4.31 g/cm^3 and has optimal microwave dielectric properties: ε_r = 26.4, Q×f = 27,300 GHz and τ_f = + 0.3 ppm/°C. Moreover, the composite is chemically compatible with Ag electrode at its sintering temperature, which makes it as a potential candidate for LTCC technology application.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ceramint.2017.06.178.

References

[1] Yoshihiko Imanak, Multilayered Low Temperature Cofired Ceramics (LTCC) Technology, Springer, Japan, 2005.
[2] M.T. Sebastian1, H. Jantunen, Low loss dielectric materials for LTCC applications: a review, Int. Mater. Rev. 53 (2) (2008) 57–90.
[3] M.T. Sebastian, R. Ubic, H. Jantunen, Low loss dielectric materials and their properties, Int. Mater. Rev. 60 (2015) 392–412.
[4] H.M. O'Bryan, J. Thomson, J.K. Plourde, A new BaO-TiO2, compound with temperature-stable high permittivity and low microwave loss, J. Am. Ceram. Soc. 57 (10) (1974) 450–453.
[5] J.H. Choy, Y.S. Han, J.T. Kim, Y.H. Kim, Citrate route to ultra-fine barium polytitanates with microwave dielectric properties, J. Mater. Chem. 5 (1) (1995) 57–63.
[6] S.Q. Yu, B. Tang, S.R. Zhang, X. Zhang, Temperature stable high-Q microwave dielectric ceramics in (1-x) $BaTi_4O_9$-x $BaZn_2Ti_4O_{11}$ system, Mat. Lett. 67 (2012) 293–295.
[7] K.C. Feng, C.C. Chou, C.S. Chen, L.W. Chu, H. Chen, Phase evolution and electrical properties of copper-electroded $BaTi_4O_9$ materials with $BaO–ZnO–B_2O_3–SiO_2$ glass system in reducing atmosphere, Ceram. Int. 39 (2013) S321–S324.

[8] Y.J. Chu, J.H. Jean, Low-fire processing of microwave $BaTi_4O_9$ dielectric with crystalline CuB_2O_4 and $BaCuB_2O_5$ additives, Ceram. Int. 39 (2013) 5151–5158.
[9] Y.I. Gormikov, Z.Y. Makarova, A.G. Belous, L.G. Gavrilova, V.M. Pashkov, V.P. Chaly, The effect of zinc-oxide addition on phase-composition and dielectric-properties of barium tetratitanate, Ukr. Khimicheskii Zhurnal 50 (12) (1984) 1243–1245.
[10] A.G. Belous, O.V. Ovchar, M. Macek-Krzmanc, M. Valant, The homogeneity range and the microwave dielectric properties of the $BaZn_2Ti_4O_{11}$ ceramics, J. Eur. Ceram. Soc. 26 (2006) 3733–3739.
[11] D.W. Kim, D.G. Lee, K.S. Hong, Low-temperature firing and microwave dielectric properties of $BaTi_4O_9$ with Zn-B-O glass system, Mater. Res. Bull. 36 (2001) 585–595.
[12] D.N. Kim, J.Y. Lee, J.S. Huh, H.S. Kim, Thermal and electrical properties of BaO–B_2O_3–ZnO glasses, J. Non-Cryst. Solids 306 (2002) 70–75.
[13] L.F. Zhou, H.X. Lin, W. Chen, L. Luo, Low-firing and microwave dielectric properties of Ba2Ti9O20 with BaO–B_2O_3–ZnO glass addition, Jpn. J. Appl. Phys. 47 (9) (2008) 7246–7249.
[14] M.Z. Long, B. Tang, S.R. Zhang, S.Q. Yu, Influence of Ba–Zn–B additives on the sintering behavior and dielectric properties of $BaNd_2Ti_4O_{12}$ ceramics, Mat. Lett. 68 (2012) 486–489.
[15] J.H. Jean, S.C. Lin, Effects of borosilicate glass on densification and properties of borosilicate glass + TiO_2 ceramics, J. Mater. Res. 14 (1999) 1359–1363.
[16] M. Liu, H.Q. Zhou, X.Y. Xu, Z.X. Yue, M. Liu, H.K. Zhu, Sintering, densification and crystallization of Ca–Al–B–Si–O glass/Al_2O_3 composites for LTCC application, J. Mater. Sci: Mater. Electron 24 (2013) 3985–3994.
[17] V.B. John, Introduction to Engineering Materials, third ed., Macmillan, Houndmills, UK, 1992.
[18] V.K. Sing, Densification of alumina and silicain the presence of a liquid phase, J. Am. Ceram. Soc. 64 (10) (1981) 133–136.
[19] S. Kemethmuller, M. Hagymasi, A. Stiegelschmitt, A. Roosen, Viscous flow as the driving force for the densification of low-temperature co-fired ceramics, J. Am. Ceram. Soc. 90 (2007) 64–70.
[20] K.G. Ewsuk, L.W. Harrision, F.J. Walczak, Sintering glass-filled ceramic composites; effects of glass properties, Ceram. Trans. Ceram. Powder Sci. II 1 (1987) 969–977.
[21] J.A. Lee, J.H. Lee, J.J. Kim, Low-temperature sintering and microwave dielectric characteristics of $Ba_2Ti_9O_{20}$ ceramics, J. Eur. Ceram. Soc. 26 (2006) 2111–2115.
[22] M. Liu, H.Q. Zhou, M. Liu, Z.X. Yue, H.K. Zhu, Low temperature sintering and properties of Ca–Al–B–Si–O glass/ceramic composites with various ceramic fillers, J. Mater. Sci: Mater. Electron 24 (2013) 2161–2168.
[23] K. Ju, H.T. Yu, L. Ye, G.L. Xu, Ultra-low temperature sintering and dielectric properties of SiO_2-filled glass composites, J. Am. Ceram. Soc. 96 (2013) 3563–3568.